

Effect of pyrolysis temperature on cobalt phthalocyanine supported on carbon nanotubes for oxygen reduction reaction

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Abstract: Cobalt phthalocyanine (CoPc)-impregnated functionalized multi-walled carbon nanotubes (CNTs) were used as nonprecious electrocatalysts for oxygen reduction reaction (ORR). The electrocatalysts were thermally treated at temperatures ranging from 450 to 850 °C, and the effect of pyrolysis temperature and their relationship to the electrocatalytic activity for ORR were investigated. Thermo gravimetric analysis, X-ray diffraction, and electron microscopy were used to study the thermal stability, crystal structure, and morphology of these catalysts. Cyclic voltammetry and rotating disk electrode results showed that CoPc/CNTs pyrolyzed at a temperature of 550 °C had the highest electrocatalytic activity for ORR, and the catalytic activity decreased with further increase in pyrolysis temperature. X-ray photoelectron spectroscopy showed decrease in functional groups at a temperature higher than 550 °C, correlating with the decreased catalytic activity. The result suggests that oxygen functional groups introduced by acid oxidation for anchoring the CoPc on CNT plays a major role in determining the electrocatalytic activity.

Keywords Oxygen reduction reaction · Carbon nanotubes · Cobalt phthalocyanine · Cathode catalyst · Fuel cells

1 Introduction

Proton exchange membrane fuel cells (PEMFC) have received considerable attention in the recent past because

of their high conversion efficiency and low operating temperature (~ 80 °C), which are favorable for their being used as power sources for portable, automobile, and stationary applications [1]. However, the low operating temperature induces serious problems in the cathode reaction, such as large overpotential for oxygen reduction reaction (ORR). In order to accelerate the rate of oxygen reduction, noble metal catalyst such as platinum is used, which is one of the obstacles hindering the commercialization of PEMFC [2]. Therefore, research and development studies aiming to reduce the amount of platinum catalyst have become increasingly intensive in recent years. There have been many approaches such as improvements in the platinum loading procedures and enhancement of the activity by alloying platinum with low cost metals [2–4]. Besides these attempts, the use of nonplatinum catalysts such as transition metal macrocycles, chalcogenides, metal carbides, and metal nitrides have been studied extensively [2, 5–7].

Among the non-noble metal catalysts, the transition metal macrocycles (N_4 -chelates) have attracted considerable attention because of their low cost and reasonable activity, and the most commonly studied are supported Fe and Co phthalocyanines [7–13]. Moreover, when these macrocycles are heat treated in an inert atmosphere at appropriate temperatures, the activity and stability are significantly enhanced [14].

Carbon black Vulcan XC-72 is the most widely used material as support for the dispersion of these macrocycles due to its good balance between conductivity and specific surface area [15]. In recent times, carbon nanotubes (CNTs) have generated intensive interest as catalyst support in fuel cells because of their unique characteristics of high electric conductivity, large surface-to-volume ratio, and corrosion resistance [8, 16]. However, CNTs are hydrophobic and inert in nature, and functionalization is

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necessary for introducing surface functional groups for anchoring the catalytically active metallic particles [17, 18]. Catalyst–support interactions play a fundamental role in catalysis, and the synthesis/post-treatment temperature may influence the functional groups responsible for anchoring the metallic phthalocyanine to the CNTs and in turn enhancing their catalytic activity.

In this study, emphasis was put on the optimization of the heat-treatment temperature for cobalt phthalocyanine (CoPc) deposited on acid-functionalized CNT support. Though there have been a few reports on the CNT-supported CoPc for oxygen reduction, these investigations have employed temperatures less than 300 °C for catalyst synthesis with the main focus of study resting on the kinetics of ORR [19, 20]. To the best of our knowledge, no study has so far evaluated the effect of pyrolysis temperature on CNT support for metal phthalocyanine.

2 Experimental

Catalyst preparation: Multi-walled CNTs (60–100 nm, Shenzhen Nano-Technologies) were functionalized by treating in a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ (1:1, v/v) solution for 4 h at 120 °C under refluxing conditions, followed by washing until the pH of the filtrated solution became neutral, and the powder thus obtained was dried overnight at 70 °C. Cobalt phthalocyanine (CoPc—Aldrich) with metal loadings of 10 wt% were prepared by impregnation method as reported in the literature [21] using CNTs as support. In brief, sulfuric acid was used to dissolve CoPc, for which functionalized CNTs were added and ultrasonicated for 5 h. Then, the slurry was added to distilled water, stirred, and filtered. The resulting precipitate was dried in vacuum oven at 70 °C and ground to a fine powder. The CoPc/CNT catalysts thus obtained were then pyrolyzed at various temperatures from 450 to 850 °C with a heating rate of 10 °C min^{-1} in a tubular furnace under high pure nitrogen at the flow rate of 0.1 L min^{-1} for 1 h.

Catalyst characterization: The thermal stability of CoPc/CNT was characterized by thermogravimetric analysis (TGA, Perkin–Elmer) which was carried out in nitrogen atmosphere, heating up to 900 °C at a rate of 10 °C min^{-1} . X-ray diffraction (XRD) patterns were measured using a Philips PW3830 diffractometer at a scan rate of 1° min^{-1} . Quantitative analyses were conducted with energy dispersive X-ray (EDX) analyzer equipped with a scanning electron microscopy (SEM, Quanta 200 FEG) operated at an acceleration voltage of 20 kV. A JEOL JEM 3010 microscope operated at 200 kV was used for the transmission electron microscopy (TEM) measurement. X-ray photoelectron spectroscopic analysis was carried out using

VG ESCALAB 220 iXL instrument at Al K α (1,486.5 eV) radiation.

Electrochemical measurements: The catalysts were electrochemically characterized by the cyclic voltammetry (CV) and linear sweep voltammetry using a CHI 600C electrochemical workstation (CH Instruments, Inc.) in a three-electrode cell housed in a BASi C3 cell stand. Rotating disk electrode (RDE) measurements were carried out with a BASi rotator system. A commercial 3 mm glassy carbon electrode was used as the working electrode substrate, Pt wire was used as the counter electrode, and Ag/AgCl 3 M KCl was used as the reference. The CoPc/CNT catalysts were applied to the surface of the glassy carbon disk electrode in the form of a constant drop of ink. The ink was prepared by mixing 2.5 mg of catalyst with 1 ml of deionized water and 0.5 ml of Nafion solution (5 wt%, Aldrich). Then, the mixture was ultrasonically blended for 1 h to obtain the catalyst ink. 2 μl of the catalyst ink was dropped on the surface of the glassy carbon disk electrode by a micropipette and was dried in air for 30 min. All electrochemical tests were carried out at room temperature in 0.5 M H_2SO_4 solution saturated and blanketed with either nitrogen or oxygen.

3 Results and discussion

It is well known that the carbon black-supported transition metal macrocycles show increase in catalytic activity when pyrolyzed at temperatures higher than 650 °C [22, 23], and the heat-treatment changes the characteristics of macrocyclic compounds and alters the active sites, morphology, and particle size, all of which significantly influence the electrocatalytic activity [22–25].

For CNTs, to achieve a favorable interaction with the deposited catalytically active particles, acid oxidation with $\text{HNO}_3/\text{H}_2\text{SO}_4$ is the most common technique used for functionalization, where oxygen-containing groups such as hydroxyl (–OH), carboxyl (–COOH), and carbonyl (>C=O), are created at the exposed CNT surface [26]. However, heat treatment of the CNTs at higher temperatures can induce loss of oxygen surface groups through their decomposition into CO and CO₂ [27], which can lead to weaker metal–support interaction with the deposited particles, resulting in lower catalytic activity. Hence, pyrolysis temperature is one of the most critical factors affecting the electrocatalytic activity for phthalocyanine deposited on CNTs.

Cobalt phthalocyanine (CoPc) with a metal loading of 10 wt% were prepared by impregnation using acid functionalized CNTs as support. Thermogravimetric analysis was performed to determine the thermal stability of CoPc/CNT, where the catalyst was heated from room temperature to

900 °C in nitrogen environment, at a temperature ramp velocity of 10 °C min⁻¹. Three relatively stable stages during heat treatment were observed as shown in Fig. 1. Stage I is from room temperature to 400 °C, in which CoPc/CNT has a stable molecular structure and only a small amount of weight is lost, because of residual water evaporation. Achar et al. [28] investigated the decomposition of CoPc pyrolyzed between 500 and 1,000 °C by gas chromatography and mass spectrometry, where the main products of pyrolysis were found to be cyanogens, hydrogen cyanide, benzonitrile, and phthalonitrile. Burgos et al. [29] reported that, with increasing heat-treatment temperature of CoPc, carbon and metal contents increased, whereas those of nitrogen and hydrogen decreased, with major loss of nitrogen having been found to occur between 550 and 700 °C. This suggests that in Stage II, which is from 400 to 600 °C, the occurrence of drastic weight loss could be due to partial decomposition of the macrocyclic structure, where low weight atoms (such as H and part of N) are lost from CoPc/CNT [11, 21, 28, 29]. In Stage III, which is from 600 to 900 °C, no additional weight loss is observed, suggesting the complete destruction of the macrocycle, leaving behind only the metallic cobalt.

The XRD patterns of CoPc/CNT heat treated at 450, 550, 650, 750, and 850 °C are shown in Fig. 2, along with the diffraction patterns of the as-received CoPc and CNT presented for a comparison. The diffraction peaks around 26°, 42°, and 54° are due to the hexagonal graphite structural planes ((002), (100), and (004), respectively) of CNT. The positions and intensities of the main diffraction lines of the as-received CoPc (curve b) are suppressed after the addition of CNT and heat treatment. The sharp peaks at 2θ of 44° and 52° obtained at higher heat-treatment

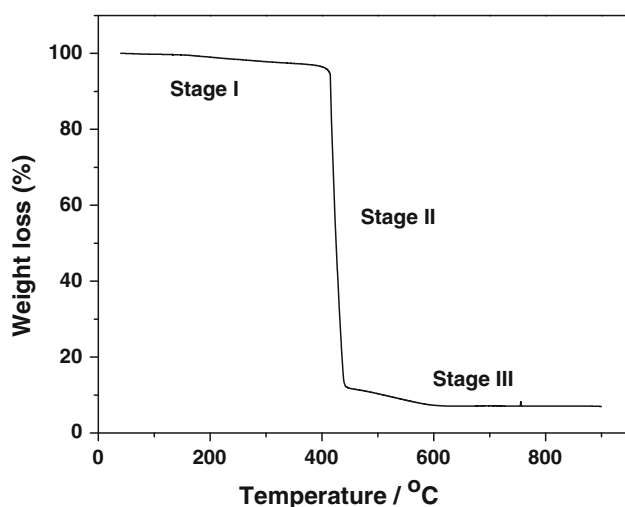


Fig. 1 Thermogravimetric curve of cobalt phthalocyanine-impregnated carbon nanotubes (CNTs) in nitrogen atmosphere at a heating rate of 10 °C min⁻¹

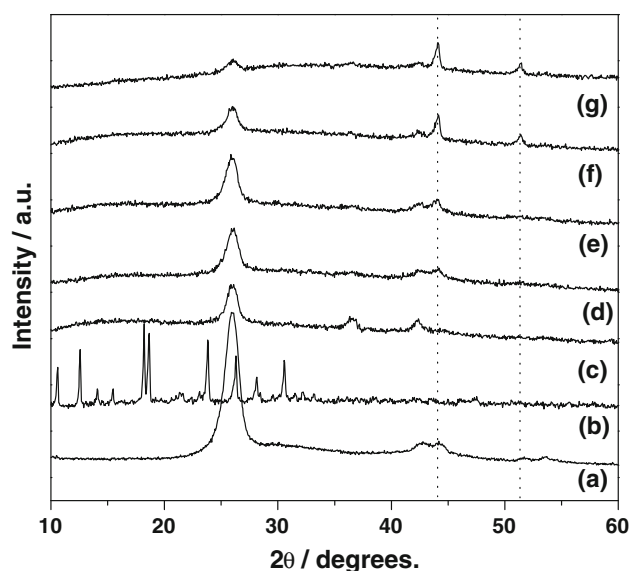


Fig. 2 X-ray diffraction patterns of CNTs (a), cobalt phthalocyanine (b), and 10 wt% CoPc/CNT heat treated at (c) 450 °C, (d) 550 °C, (e) 650 °C, (f) 750 °C, and (g) 850 °C

temperatures of 750 and 850 °C are due to the crystalline Co, as high-treatment temperatures provide the ambience for agglomeration and formation of crystalline phase. As reported by Lalande et al. [30], the metallic Co particles begin to form at around 550 °C, and the growth of Co particles occurs with increase of the pyrolysis temperature up to 900 °C.

Figure 3 shows a representative SEM images for 10 wt% CoPc nanoparticles supported on carbon nanotubes, which was heat treated at 550 °C along with the EDX spectrum. As can be seen from the figure, aggregates of CoPc particles are dispersed on CNT support, and the EDX spectroscopy confirmed the presence of Co in the catalyst. Figure 3b shows the corresponding TEM images, where CoPc particles are in the range of 10–20 nm dispersed on the surface of CNTs.

The electrocatalytic activity of 10 wt% CoPc/CNT pyrolyzed at various treatment temperatures were studied by voltammetry in 0.5 M H₂SO₄ solution saturated with nitrogen (for blank) or oxygen for oxygen reduction experiments. Typical cyclic voltammograms obtained for CoPc/CNT at a scan rate of 100 mV s⁻¹ in nitrogen- and oxygen-saturated acidic solution for the catalyst pyrolyzed at 450, 550, 650, and 750 °C are shown in Fig. 4. As evident from the figure that cathodic current density increased for all the catalysts in oxygen-saturated solution, confirming the reduction of oxygen at CoPc/CNT. The catalyst showed an increase in cathodic current and a slight positive shift in onset potential on increasing the pyrolysis temperature from 450 to 550 °C, whereas further increase in the treatment temperature resulted in lower reduction current.

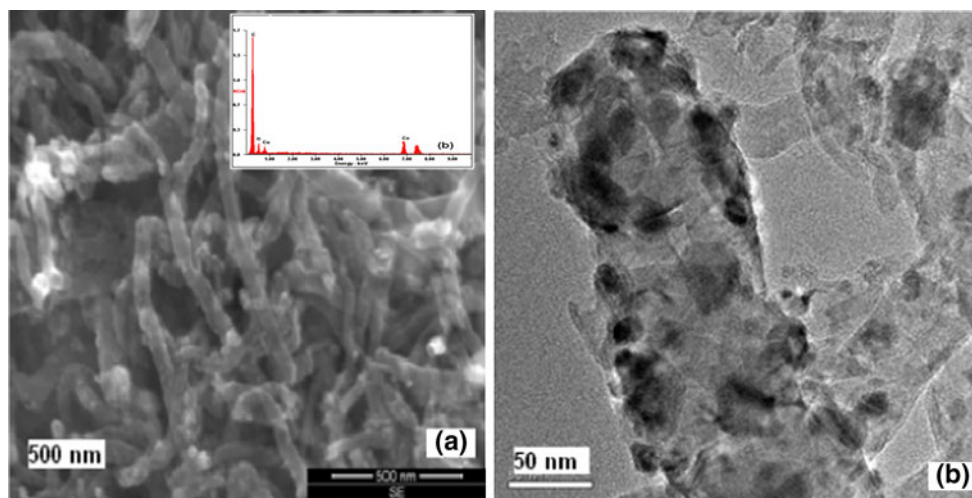
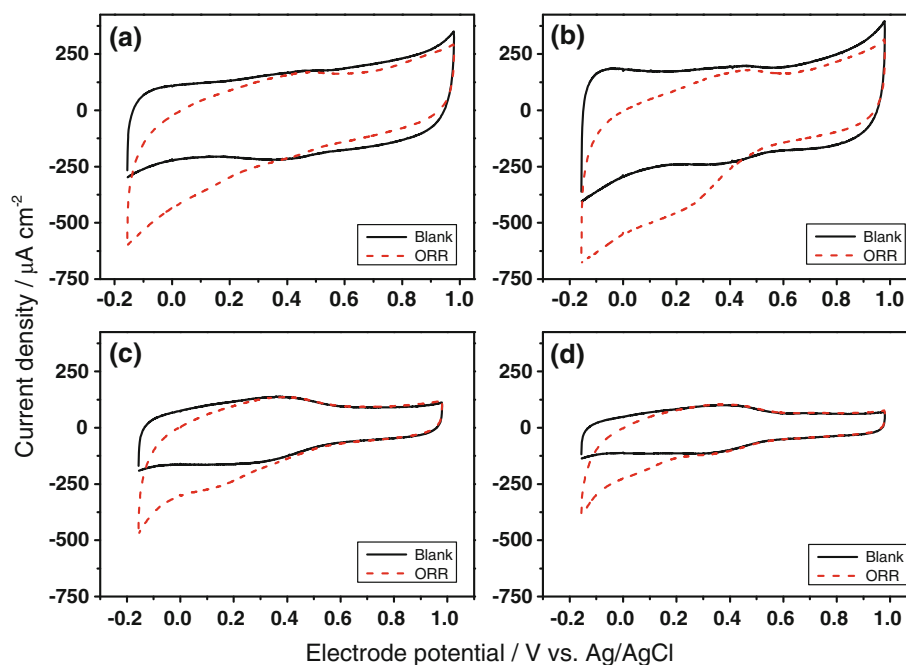


Fig. 3 **a** Scanning electron micrograph of 10 wt% CoPc/CNT pyrolyzed at 550 °C, with the *inset* showing the EDX plot, and **b** the corresponding transmission electron micrograph

Fig. 4 Cyclic voltammograms of CoPc/CNT recorded at a scan rate of 100 mV s⁻¹ in 0.5 M H₂SO₄ saturated with nitrogen and oxygen for the catalyst pyrolyzed at **(a)** 450 °C, **(b)** 550 °C, **(c)** 650 °C, and **(d)** 750 °C



Linear sweep voltammograms performed at a pseudo steady-state scan rate of 1 mV s⁻¹ in the potential range of 1–0.2 V (vs. Ag/AgCl) for CoPc/CNT catalyst pyrolyzed at various temperatures are shown in Fig. 5, along with the unpyrolyzed catalyst. As evident from the figure, the highest current density was obtained when the catalyst was pyrolyzed at 550 °C (curve b), and the unpyrolyzed CoPc/CNT showed very low reduction current (curve e). The onset potential and current density at 0.4 V were 0.52 V and 15.5 μA cm⁻², respectively, for the catalyst pyrolyzed at 450 °C, whereas the current density and onset potential decreased to 3.5 μA cm⁻² and 0.42 V, respectively, when the heat-treatment temperature was 750 °C. The highest

onset potential of 0.53 V and current of 35 μA cm⁻² were obtained for the catalyst heat treated at 550 °C. Hence, the optimum heat-treatment temperature that displayed the highest electrochemical activity for the ORR with CoPc/CNT catalyst is 550 °C.

This is further confirmed by the rotating disk electrode studies performed in an oxygen-saturated solution of 0.5 M H₂SO₄ obtained at 400 rpm comparing with CoPc/CNT pyrolyzed at 550 and 650 °C. Figure 6 shows the typical current density–potential curve recorded at a scan rate of 5 mV s⁻¹. As evident from the figure, the curve of CoPc/CNT at 550 °C shows 100 mV shift in terms of onset to positive potentials compared to that of CoPc/CNT at

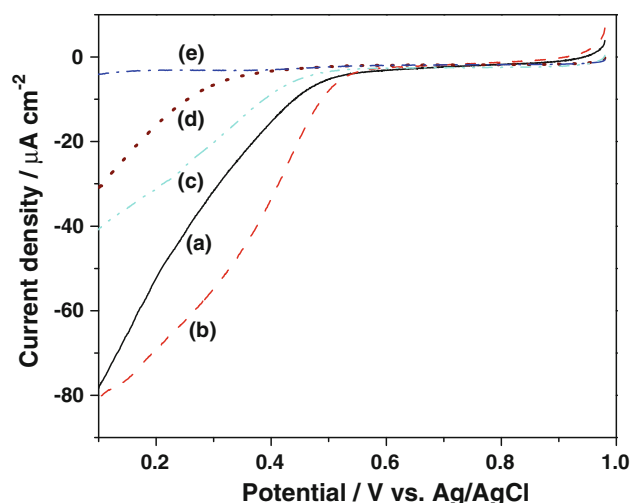


Fig. 5 Comparison of linear sweep voltammograms recorded at 1 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ saturated with oxygen for 10 wt% CoPc/CNT heat treated at (a) 450, (b) 550, (c) 650, (d) 750 °C, and (e) CoPc/CNT without heat treatment

650 °C. Current density values at 0.2 V for the CoPc/CNT catalysts heat treated at 550 and 650 °C are 360 and 235 $\mu\text{A cm}^{-2}$, respectively. This confirms that the activity of CoPc/CNT at 550 °C is higher than that of CoPc/CNT at 650 °C. The oxygen reduction potential E_{O_2} (defined as the voltage at which reduction current density of $-10 \mu\text{A cm}^{-2}$ is reached) of CoPc/CNT is 0.54 V, and is similar to CoPc-based carbon catalysts reported in the literature [31].

For comparative purpose, Pt/CNT (10 wt%) prepared by impregnation–reduction method [26] was studied by RDE at 400 rpm in oxygen saturated $0.5 \text{ M H}_2\text{SO}_4$ at a scan rate of 5 mV s^{-1} , and the voltammogram is shown as inset in

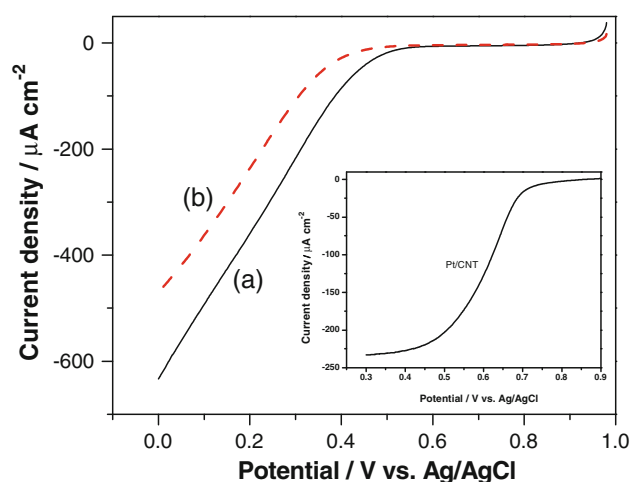


Fig. 6 Rotating disk electrode measurements of oxygen reduction obtained at 5 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ and 400 rpm for CoPc/CNT heat treated at (a) 550 °C and (b) 650 °C. Inset shows the ORR for Pt/CNT catalyst

Fig. 6. As evident from the figure, the onset of oxygen reduction at CoPc/CNT catalyst starts at a higher overpotential ($\sim 175 \text{ mV}$) than that of Pt catalyst. However, transition metal phthalocyanines are known to be selective catalysts, do not poison in the presence of methanol, and they have good tolerance toward carbon monoxide thus making them a good alternative candidate to platinum [4, 5].

To investigate the short-term stability of CoPc/CNT catalyst pyrolyzed at 550 °C, we performed continuous potential cycling between 1 and 0.2 V for 50 cycles in oxygen-saturated $0.5 \text{ M H}_2\text{SO}_4$ at room temperature. The study of stability of CoPc/CNT catalyst displayed in Fig. 7 showed no drastic change in voltammetric response before and after the cycling, considering the rapid degradation observed by Baranton et al. [32] for the carbon-supported phthalocyanine catalyst. After the potential cycling, only a slight shift in the onset potential leading to a small decrease in the current density was observed for CoPc/CNT.

As mentioned earlier, carbon black-supported CoPc catalysts showed the highest activity at a pyrolysis temperature of $\geq 650 \text{ °C}$ [e.g., 22, 23], whereas CNT-supported CoPc showed lower catalytic activity at a higher pyrolysis ($\geq 650 \text{ °C}$) temperature. Hence, X-ray photoelectron spectroscopy was performed to get better understanding on the surface composition and types of moieties existing on the CoPc/CNT, when the catalysts were heat treated at 550 and 650 °C. Figure 8a–d shows the XPS survey spectra and regional spectra of Co $2p_{3/2}$, N 1s, and O 1s for heat-treated CoPc/CNT. As seen from survey spectra, the N 1s peak of the CoPc/CNT catalyst has lower intensity than that of C 1s peak because of the atomic ratio N/C ($=8/32$) in the CoPc

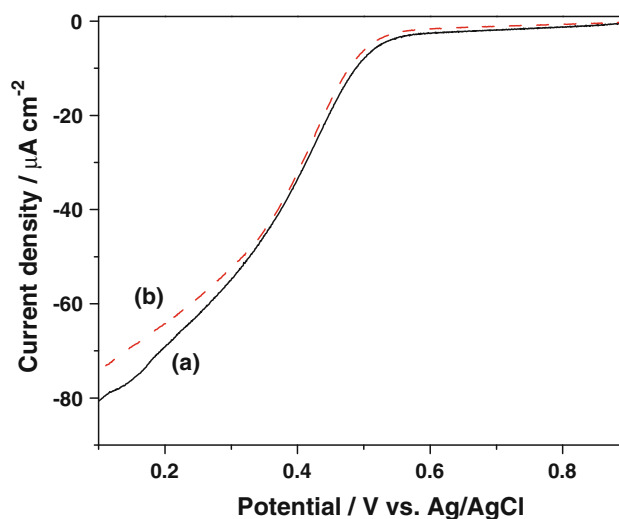


Fig. 7 Study of electrode stability: voltammograms for oxygen reduction on CoPc/CNT catalyst pyrolyzed at 550 °C before (a) and after (b) continuous potential cycling for 50 cycles at scan rate of 50 mV s^{-1} in oxygen-saturated $0.5 \text{ M H}_2\text{SO}_4$ at room temperature

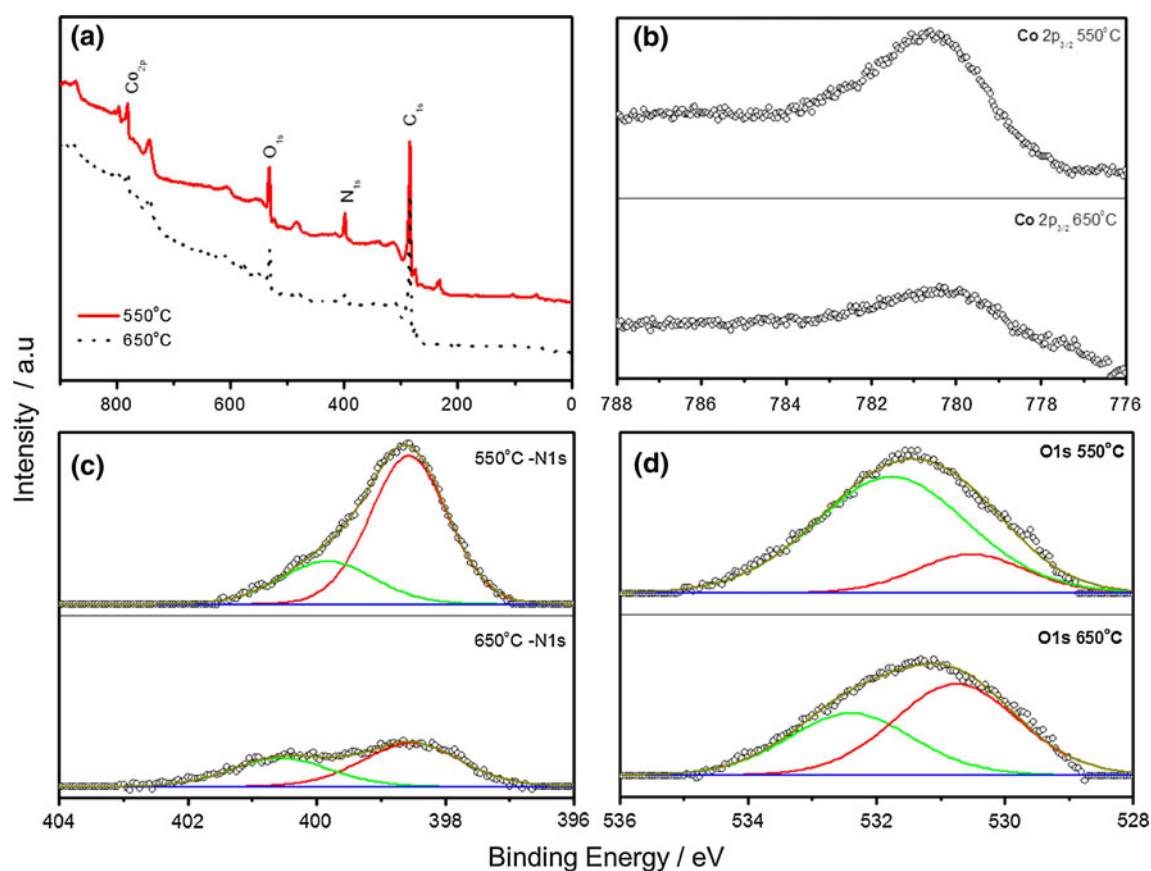


Fig. 8 X-ray photoelectron spectra of CoPc/CNT subjected to pyrolysis at 550 and 650 °C showing **a** the survey spectra, **b** Co 2p_{3/2}, **c** N 1s, and **d** O 1s regions

molecule. The elemental surface compositions of all the components derived from XPS for the catalysts heat treated at 550 and 650 °C are given in Table 1. As evident from the molecular structure of metal phthalocyanine [19, 33], the Co atom is located at the ligand environment of the nitrogen-enriched structure of the phthalocyanine ring. The Co 2p_{3/2} peak at binding energy 780.8 eV is attributed to the bonding between the cobalt atom and the four central nitrogen atoms in the phthalocyanine molecule [34]. The N 1s peak of the CoPc consists of the broad peak at 399 eV and a weaker feature at higher binding energies. The main peak can be ascribed to the two chemically nonequivalent nitrogen atoms of the organic molecule, while the weaker peak is attributed to the satellites of the main peak [35]. The deconvolution of O 1s spectrum showed two peaks, which can be attributed to oxygen being double-bonded to carbon (O=C) at 531.4 eV, and oxygen being single-bonded to carbon (C–O–C) at 533.2 eV [26]. As shown in Table 1, heat treatment of CoPc/CNT at 650 °C induces a significant decrease of the oxygen-to-carbon ratio, and induces a decrease in nitrogen and Co contribution with an increase of carbon. The decreases in the relative percentages of the elemental compositions and the peak intensity

(shown in Fig. 8) of the catalyst heat treated at 650 °C suggest that the functional groups might have been lost and Pc ring might have been damaged at higher pyrolysis temperature, resulting in lower catalytic activity. As reported by Bezerra et al. [5], the bulk N content also decreases as the pyrolysis temperature is increased, and metallic Co particles begin to agglomerate at higher temperatures (as evident from the XRD patterns at Fig. 2).

As reported by Kalvelage et al. [22], carbon with pyrolyzed nitrogen-free complex compounds (e.g., cobaltocene) showed almost no catalytic activity, which points to the importance of the nitrogen and the nitrogen fragments for catalytic activity against oxygen reduction. Hence, the highest catalytic activity obtained with a treatment temperature of 550 °C, could be due to the optimum bonding of nitrogen, with cobalt providing the favorable active site with ideal particle size for the reduction of oxygen. Moreover, the surface of the CNT support contains oxygen functional groups, and defects introduced by acid oxidation might act as the most complementing support for the deposition and dispersion of CoPc at 550 °C. The disorder in the graphitic layer and the presence of exposed edge plane defects due to CNT functionalization and

Table 1 XPS surface atomic concentration of cobalt phthalocyanine supported on CNTs pyrolyzed at 550 and 650 °C

Sample, pyrolysis temperature	C/%	O/%	N/%	Co/%
CoPc/CNT, 550 °C	72.17	17.71	8.22	1.90
CoPc/CNT, 650 °C	89.01	7.48	2.83	0.70

nitrogen functionalities are important factors influencing the electrocatalysis for oxygen reduction [12]. As the pyrolysis temperature is increased, the oxygen functional groups anchoring the metallic particles on CNT surface are weakened, and hence, there is a decrease in the catalytic activity.

From the above observation, it can be concluded that, when acid functionalized CNTs are used as an alternative support for CoPc, the maximum catalytic activity for ORR is obtained when the pyrolysis temperature is 550 °C. Future studies are planned to elucidate the catalytic performance in a single fuel cell.

4 Conclusions

In this study, CoPc/CNT prepared by impregnation was heat treated at various temperatures: 450, 550, 650, 750 and 850 °C, and characterized by physical and electrochemical techniques to find the optimum pyrolysis temperature for the maximum activity of ORR. The results showed that the heat-treatment temperature plays an important role in determining the electrochemical activity of the ORR, and the pyrolysis temperature of 550 °C showed the highest electrocatalytic activity for CoPc supported on carbon nanotubes. Oxygen functional groups introduced by acid oxidation for anchoring the metal deposits on CNTs play a major role in determining the electrocatalytic activity.

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